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Unusual behavior in the upper critical magnetic fields of the ambient-pressure organic superconductor: κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [where BEDT-TTF represents bis(ethylenedithio)tetrathiafulvalene]

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We report a determination of the temperature dependence of the upper critical magnetic fields H_{c2} for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, with the use of dc-magnetization measurements that show a well-defined diamagnetic onset. We find large slopes of −20 and −2.2 T/K for **H**$\|ac$ and **H**$\|b$, respectively, which lead to coherence lengths of 37 and 4 Å. There is unusual structure in the critical fields and a possible dimensional crossover at $T/T_c \sim 0.97$ for **H**$\|ac$. Neither the slopes nor the structure are observable in the superconducting transition measured by ac magnetoresistance, which exhibits strong magnetic-field broadening similar to that of the high-T_c copper oxide superconductor YBa$_2$Cu$_3$O$_{7-\delta}$. We find a strong depression of T_c, as large as 1.2 K, when the sample is rapidly cooled.

Recently we reported[1,2] the existence of superconductivity at 11.60 ± 0.01 K (diamagnetic onset) at ambient pressure in the organic charge-transfer salt κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, where BEDT-TTF is the radical-cation organic donor molecule *bis*(ethylenedithio)tetrathiafulvalene and [N(CN)$_2$]$^-$ is the dicyanamide anion. This is the highest transition temperature yet achieved for an organic superconductor. In this paper, we report a determination of the temperature-dependent upper critical magnetic fields H_{c2} for this salt. Our results were derived from dc-magnetization measurements, and they show slopes much larger than those generally reported for organic superconductors. We find unexpected features in the critical-field behavior very near T_c. Resistive measurements of the transition in a magnetic field show strong broadening, similar to that of the high-temperature oxide superconductors, with no obvious feature associated with the diamagnetic onset. Unlike the data reported for the high-temperature superconductors, the shape of the resistive transition changes character at high fields. Finally, we report a dramatic effect on the transition temperature with increase in the cooling rate: a depression of 1.2 K for samples cooled to 4.2 K in less than 5 min. This cooling-rate effect may be related to "quenched-in" disorder.

In the orthorhombic-unit-cell setting previously described[1] for this salt, the layers of the organic donor molecules lie parallel to the *ac* plane (the plane of highest electrical conductivity), and each donor-molecule layer is segregated along the *b* axis (an axis of lower electrical conductivity) by a layer of a polymeric network of the anions. Three single crystals, synthesized by the electrocrystallization techniques described elsewhere,[3] were used in these experiments. One crystal was used for transport measurements, and the other two for magnetization measurements. ac magnetoresistance up to 8 T was measured by a four-probe technique with gold wires attached by silver paste along the long axis of the plate in the *ac* plane of the crystal. The typical measuring current was 0.1 mA at a frequency of 17 Hz. dc magnetization measurements up to 4 T were carried out with the use of a superconducting quantum interference device magnetometer.

Figure 1 shows the temperature dependence of the field-cooled (FC) magnetization in 1 T and 5 Oe near the superconducting transition temperature for **H**$\|b$. For 1 T, the zero-field-cooled (ZFC) magnetization curve, i.e., the magnetization measured by first cooling the sample in zero field and then applying a magnetic field and collecting data while warming, is also included. The identical behavior of the FC and ZFC curves indicates that the magnetization in this temperature range is reversible. The observed linear temperature dependence of the magnetization below T_c is expected from three-dimensional (3D) Ginzburg-Landau theory, and we define the nucleation temperature $T_c(H)$ as the intercept of the linear

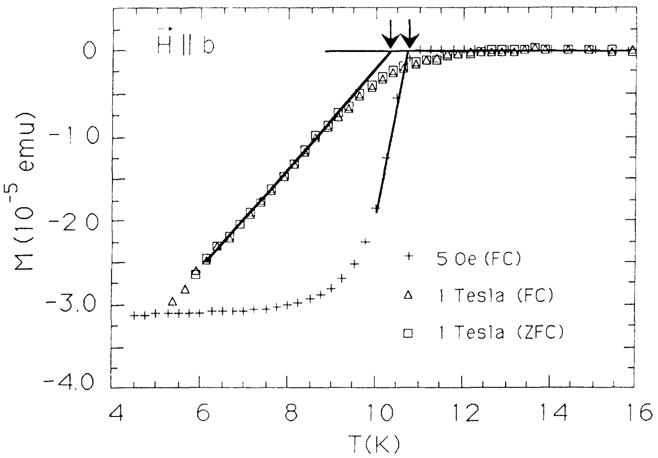

FIG. 1. Temperature dependence of the magnetization in 1 T (field cooled and zero-field cooled) and 5 Oe (field cooled) for **H**$\|b$. The arrows designate the mean-field transition temperature for the two magnetic fields.

extrapolation of the magnetization in the superconducting state with the linear extrapolation of the normal-state base line. This extrapolated T_c is, due to some rounding, lower than the diamagnetic onset at 11.6 K. A comparison with the 5 Oe curve data shows a clear depression of T_c with increasing magnetic field. The curvature in $M(T)$ at 1 T near the transition may be due to diamagnetic fluctuations or sample inhomogeneities. We find qualitatively similar results for $\mathbf{H}\parallel ac$ (where parallel ac represents an arbitrary direction parallel to the ac plane).

The H_{c2} phase diagram obtained from such measurements for $\mathbf{H}\parallel b$ and $\mathbf{H}\parallel_{ac}$ is shown for two different single-crystal specimens (crystals A and B) in Fig. 2. Crystal A was slowly cooled to 4 K over a period of hours, whereas crystal B (with only $\mathbf{H}\parallel b$ represented) was quenched to ~4 K in <5 min. We see an approximately constant downward displacement in the upper critical field for the quenched specimen (crystal B) compared with the slow cooled specimen, with zero-field T_c's of 9.6 ± 0.05 and 10.8 ± 0.05 K. After warming followed by slow cooling, the zero-field T_c of crystal B increased to 10.7 ± 0.1 K. The crystallographic structure of κ-(BEDT-TTF)$_2$Cu-[N(CN)$_2$]Br has partial disorder in the terminal ethylene groups of the BEDT-TTF molecule which decreases with decreasing temperature.[2] We speculate that the high-temperature crystallographic disorder is frozen in by rapid cooling, thus decreasing T_c.

The inset in Fig. 2 presents an expanded scale of the phase diagram near the zero-field T_c for crystal A. A very shallow tail is observed in H_{c2} in the vicinity of the zero-field transition temperature. In this region, the slopes dH_{c2}/dT are -0.5 and -0.04 T/K for $\mathbf{H}\parallel ac$ and $\mathbf{H}\parallel b$, respectively. This shallow slope is followed by a rapid increase in H_{c2} from about 0.05 T to 1 T in both field directions, beginning near 10.7 and 10.35 K with slopes -4.7 and -10 T/K for $\mathbf{H}\parallel ac$ and $\mathbf{H}\parallel b$, respectively. A further abrupt change in slope is seen for each field direction at $H \sim 1$ T. For $\mathbf{H}\parallel ac$, the H_{c2}^{ac} curve bends upward beginning near 10.5 K with slope -20 T/K; for $\mathbf{H}\parallel b$, the H_{c2}^{b} curve bends downward beginning near 10.25 K with slope -2.2 T/K. These several changes in slope are remarkable because they all occur within an interval of 0.55 K below the zero-field T_c. We did not investigate the anisotropy of the critical field within the ac plane. The calculated Fermi surface of this material suggests that the conductivity within this plane is nearly isotropic.[1]

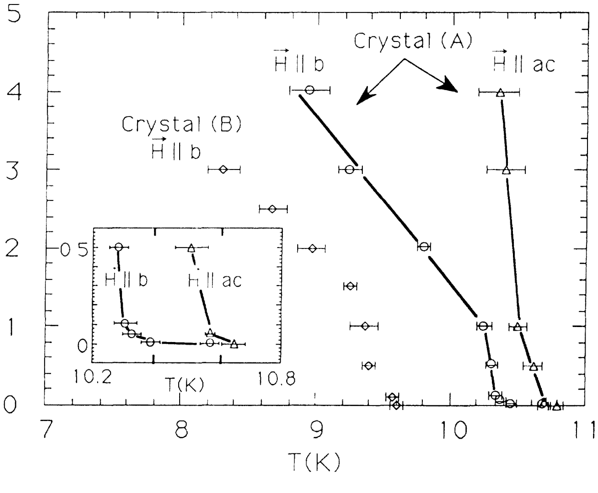

FIG. 2. Temperature dependence of the magnetically determined upper critical fields for $\mathbf{H}\parallel ac$ and $\mathbf{H}\parallel b$ for an unquenched crystal (A), and $\mathbf{H}\parallel b$ for a quenched crystal (B). Inset: Low-field part of the phase diagram for crystal A.

The initial slopes of H_{c2} near T_c yield an anisotropy ratio H_{c2}^{ac}/H_{c2}^{b} of ~13, which is comparable to those reported for other quasi-2D organic superconductors with higher electrical conductivity in the plane of the organic donor molecules.[3–5] The further large increase in slope for H_{c2}^{ac} near 1 T leads to a rapid increase of the anisotropy ratio with decreasing temperatures, reaching a value of ~80 at 10.35 K, the lowest temperature available for a comparison. This implies a decrease in dimensionality of the superconductor and suggests that the abrupt change in slope near 10.5 K represents a crossover from anisotropic bulk 3D superconductity to Josephson-coupled 2D superconductivity. A similar change in slope, identified as a 3D-2D crossover, has been reported to occur near $T/T_c \approx 0.9$ for the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ superconductor.[6] From the slope of -20 T/K for $\mathbf{H}\parallel ac$, we obtain by a Ginzburg-Landau (GL) extrapolation an estimate of the zero-temperature critical field, $H_{c2}^{ac}(0) \approx 216$ T, which far exceeds the Pauli limiting value of $H_p \approx 20$ T. We observe for $\mathbf{H}\parallel b$ that the approximately linear curve for H_{c2} with slope -2.2 T/K extrapolates very near to the zero-field T_c. From this extrapolation, we obtain $H_{c2}^{b}(0) \approx 24$ T, which is close to the Pauli limit.

These values of $H_{c2}(0)$ yield the GL coherence lengths $\xi_{ac}(0) \approx 37$ Å and $\xi_b(0) \approx 4$ Å. $\xi_b(0)$ is much smaller than the separation of the superconducting layers, $b/2 \sim 15$ Å. If the 3D-2D crossover occurs when $\xi = 15$ Å, we estimate the crossover temperature from GL theory to be $T_{c0}/T_c = 1 - [\xi_b(0)/15]^2 \sim 0.93$ or $T_{c0} = 10.0$ K, which is close to the break in H_{c2}^{ac} at 10.5 K.

Figure 3 shows the resistive transition for magnetic fields $\mathbf{H}\parallel ac$ and $\mathbf{H}\parallel b$ up to 8 T. In zero field, the resistive onset is 12.5 K, and zero resistance occurs at 10.5 K. In the presence of magnetic fields with $\mathbf{H}\parallel ac$, the resistive onset temperatures remain nearly unchanged for fields up to 8 T, but the zero-resistance points shift to lower temperatures, leading to a "fan-shaped" broadening of the transition curves. This type of behavior has been consistently observed in the high-T_c superconductors like YBa$_2$Cu$_3$O$_{7-\delta}$ where it has been partly attributed to mechanisms[7] relating to flux flow, flux creep, and Josephson junctions near the low-temperature region of the resistive tail and fluctuations near the onset temperature. However, the major cause of the broadening remains to be explained. With $\mathbf{H}\parallel b$, a similar fan-shaped broadening occurs for $H < 1$ T. However, with increasing applied fields, the resistive transition changes from the fan-shaped characteristic to a situation in which the entire transition curve appears to shift to lower temperatures. Near the onset temperatures, the magnetoresistance curves are concave downward for $H < 1$ T and slightly concave upward for $H > 1$ T. This crossover in shape near 1 T in the magnetoresistance for $\mathbf{H}\parallel b$ corresponds to the abrupt change

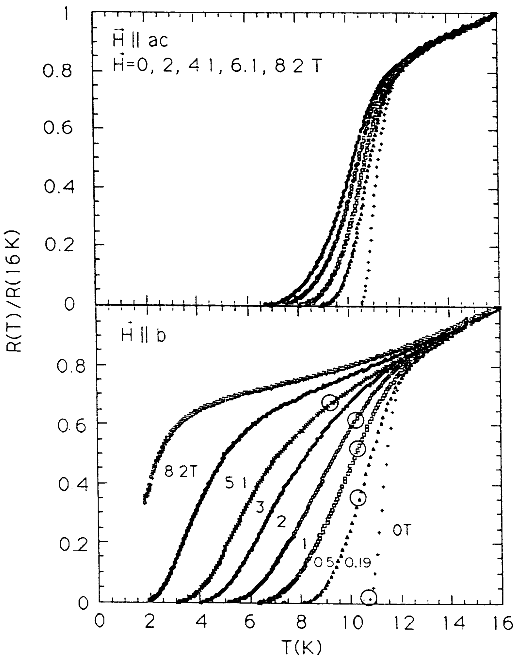

FIG. 3. Temperature dependence of the normalized resistance for **H**∥*ac* and **H**∥*b*. Open circles show the corresponding magnetically determined nucleation temperatures for **H**∥*b*.

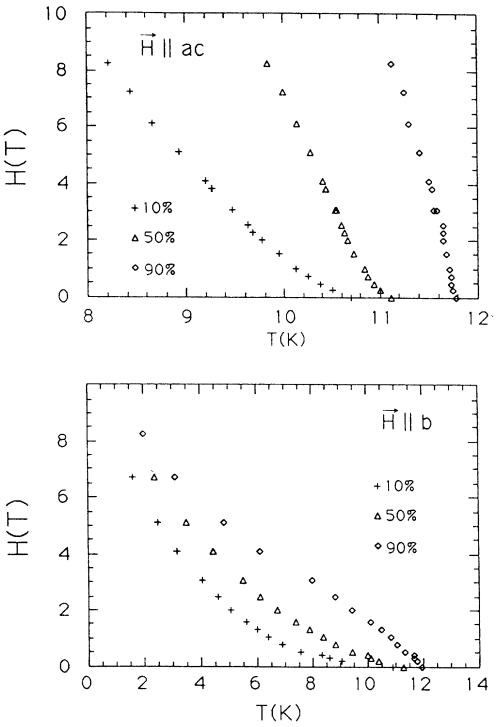

FIG. 4. *H* vs *T* derived from the data in Fig. 3 for **H**∥*ac* and **H**∥*b* from the 10%, 50%, and 90% superconducting resistive transitions.

in the slope of H_{c2}^{b} near 1 T and 10.25 K.

The determination of H_{c2} from electrical transport measurements of superconductors with broad superconducting transitions can lead to large ambiguities, as shown by Welp *et al.*[8] for the high-T_c oxide superconductor $YBa_2Cu_3O_{7-\delta}$. Figure 4 shows H_{c2} vs T curves for **H**∥*ac* and **H**∥*b* obtained from transport measurements by taking the 10%, 50%, and 90% points on the resistive superconducting transitions. These curves are qualitatively different from the phase diagram measured by dc magnetization, and the various resistive criteria for T_c give very different results for H_{c2}. For **H**∥*ac*, the initial slopes vary from -2.3 to -19 T/K and for **H**∥*b* the initial slopes vary from -0.15 to -0.85 T/K. None of the curves show the interesting structure seen in the magnetic data. Further insight into the comparison of the two methods is provided by the open circles on the lower panel of Fig. 3, indicating the position on the resistance curves of the diamagnetic transition. At zero field, the transition occurs near the zero of resistance, as expected in comparing a bulk measurement with a "path-sensitive" measurement. In field, the diamagnetic transition shifts to near the top of the resistivity curve, indicating that a dissipative mechanism (i.e., flux flow), exists in the superconducting state. The presence of this mechanism makes resistivity measurements ineffective for determining the onset of superconductivity.

Our midpoint (50%) diagrams very much resemble the midpoint curves of the magnetoresistance measurements reported for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by Oshima *et al.*,[6] except that our slopes are about a factor of 2–3 larger. The initial slopes of ~ -2 and ~ -0.1 T/K for the high- and low-field directions, respectively, reported by Oshima *et al.* are rather typical of those determined from magnetoresistance measurements reported for all other organic superconductors. On the other hand, Graebner *et al.*[9] have recently reported much larger initial slopes, -16 and -0.75 T/K, respectively, for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ from specific-heat measurements. Our magnetic determinations of H_{c2} indeed show that very large slopes occur near T_c for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, but the slopes *evaluated at* T_c are very small. Furthermore, our results show that, although some features of the phase diagram are revealed by magnetoresistance, there is no apparent "correct" choice of criteria in magnetoresistance measurements which corresponds to values of H_{c2} obtained from dc magnetization measurements.

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[1] A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 2555 (1990).

[2] J. M. Williams, A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, and M. H. Whangbo, in *Proceedings of the International Conference on Organic Superconductors, South Lake Tahoe, CA, 1990* (Plenum, New York, in press).

[3] H. Schwenk, S. S. P. Parkin, V. Y. Lee, and R. L. Greene, Phys. Rev. B **34**, 3156 (1986).

[4] L. N. Bulaevskii, V. B. Ginodman, and A. V. Gudenko, Pis'ma Zh. Eksp. Teor. Fiz. **45**, 355 (1987) [JETP Lett. **45**, 451 (1987)].

[5] H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kanamoto, and J. Tanaka, Chem. Lett. **1988**, 55.

[6] K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 730 (1988).

[7] For a review see A. P. Malozemoff, T. K. Worthington, E. Zeldov, N. C. Yeh, M. W. McElfresh, and F. Holtzberg, in *Strong Correlations and Superconductivity,* Springer Series in Physics, Vol. 89, edited by H. Fukuyama, S. Maekawa, and A. P. Malozemoff (Springer-Verlag, Heidelberg, 1989), p. 349.

[8] U. Welp, W. K. Kwok, G. W. Crabtree, K. G. Vandervoort, J. Z. Liu, Phys. Rev. Lett. **62**, 1908 (1989).

[9] J. E. Graebner, R. C. Haddon, S. V. Chichester, and S. H. Glarum, Phys. Rev. B **41**, 4808 (1990).